<u>Microlithography Projection Objective with Crystal Lens</u>

The invention relates to a microlithography projection objective with at least one crystal lens, wherein the objective is designed in particular for a high numerical

5 aperture and with immersion or optical near field.

From publications such as

Bruce W. Smith et al. Optical Microlithography XVII

10 Proc. SPIE <u>5377</u> (2004), p 273 –284;

Bruce W. Smith et al. Optical Microlithography XVI,
Proc. SPIE <u>5040</u> (2003), p 679 –689;

15 John H. Burnett et al. "High Index Materials for 193 nm and 157 nm Immersion
lithography"
Int`l Symp. on Immersion & 157 nm Lithography, Vancouver 8/2/04 (NIST/ Corning
Tropel)

20 and patent applications such as
WO2004/019 128 A2,
or, commonly owned with this application:
US 6,717,722 B,
US Ser. No. 10/734,623 filed 15 Dec. 2003,
25 US Ser. No. 60/530,623 filed 19 Dec. 2003,
US Ser. No. 60/530,978 filed 22 Dec. 2003,
US Ser. No. 60/544,967 filed 13 Feb. 2004,
US Ser. No. 60/568,006 filed 04 May 2004,
US Ser. No. 60/592,208 filed 29 July 2004,
30 US Ser. No. 60/591,775 filed 27 July 2004,
US Ser. No. 60/612,823 filed 24 Sept 2004,
DE 10 2004 051 730.4   filed 22 Oct. 2004

some information about this art can be gathered.

Of these, e. g. WO 2004/019 128 A2, US 10/734,623,
US 60/592,208, US 60/591,775 and US 60/612,823 show objective designs which can
be optimized by and combined with the use of materials and teachings according to
this application.

Suitable immersion liquids are inter alia described in US 60/568,006 or DE 10 2004
051 730.4.

PCT application entitled "Microlithography Projection Objective with Crystal
Elements", inventor Karl-Heinz Schuster, filed on December 10, 2004, internal
reference 04213 P PCT, assigned to the same assignee teaches the case of certain non-
cubic crystals in this context. Each can be combined with this invention.

All cited documents are incorporated into this application by reference in their
entirety.

Their citation in no way constitutes any declaration on their relevance for this
application, and the list certainly is incomplete and many more publications relate to
this art.

Crystal lenses consisting in particular of calcium fluoride (fluorspar) or other fluorides
have been used until now as a means to achieve a sufficient transmittance at
wavelengths below 200 nm and down to, e.g., 126 nm, and also to achieve a chromatic
compensation by using fluoride lenses particularly in combination with lens elements
of quartz glass. As a rule, these arrangements involved the use of several crystal
lenses in the objective, with diameters exceeding 10 cm and with a combined thickness
of the order of 10 cm, where the lenses had to be arranged at different places in the
objective, including in particular locations close to the pupil and close to the object.
Because of the resulting requirements regarding the homogeneity of the mono-crystals
only lenses of calcium fluoride were realized in actual practice.

The same material is also known to be suitable for lenses close to a field plane because of its higher radiation resistance associated with a lower degree of compaction compared to quartz glass.

5   To reduce the achievable structure widths in lithography systems, the first approach that always comes to mind is to use shorter wavelengths. However, the shorter the wavelength, the more difficult it becomes to find suitable immersion materials and lens materials with a high refractive index. Attempts have therefore been made to stay with longer wavelengths but find materials that have an even higher refractive index to

10   compensate for the disadvantage of the longer wavelength. For example, in order to obtain the same level of resolution with light of 248 nm as with light of 193 nm, the aperture has to be larger by a factor of 1.285. According to the formula $NA = k_1\lambda/(\text{structure width})$, i.e., $NA = 0.3 \times 248.338\,\text{nm}/50\,\text{nm}$, a resolution of 50 nm would require a refractive index of at least 1.49 if a value of 0.3 has been selected for

15   k_1.

Since quartz glass (fused silica, SiO_2) has a refractive index of 1.506235 at a wavelength of 248 nm, a resolution of 50 nm for $k_1 = 0.285$ could be achieved with the available standard material SiO_2. However, the next node at 45 nm is not attainable

20   without a change of material.

Consequently, it is an object of the invention to propose lens materials with a particularly high refractive index for lenses in the area near the image plane of an objective of the kind described in generic terms in the introductory paragraph,

25   including suitable protector plates or other elements. If the refractive index is higher than for quartz glass, it is also possible to use materials whose other properties are less ideal, such as calcium fluoride, for individual elements with a thickness of a few millimeters to centimeters.

30   Solutions to the foregoing task are proposed in accordance with the independent claims, with advantageous further developed embodiments being proposed in accordance with the subordinate claims and in accordance with the description in its entirety.

In accordance with the invention, a material has been found which has a higher refractive index and can meet all other requirements for lithography applications. As a prerequisite, the material needs to be sufficiently isotropic. However, an intrinsic

5   birefringence in the deep ultraviolet range near the absorption edge has to be tolerated. As a rule, the further away the absorption edge, the smaller are the values of the intrinsic birefringence. A particularly advantageous selection is achieved if the intrinsic birefringence crosses the zero level at the wavelength being used for the lithography application.

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For the 45 nm node and a wavelength of 248.338 nm, sodium chloride (NaCl) was found to be suitable, which at this wavelength has a refractive index of 1.657766. Its intrinsic birefringence is small enough that no compensation is necessary. As it is sufficient to make the last optical element or individual ones among the last elements

15   in the objective from this material, all of the other elements can be of quartz glass, which is preferred. However, one could also use, e.g., calcium fluoride.

The invention will be further explained hereinafter with reference to the drawings, wherein Figures 1 to 8 schematically illustrate sections through the lenses near the

20   image plane of a projection objective according to the invention, including the immersion area and the wafer or another object being exposed to the projection.

The following symbols are used consistently in the drawings:

25   AS =   aperture stop / system aperture

P   =   protector plate / protective element

I   =   immersion

W   =   wafer, or the object to be exposed in the image plane

FL =   fluid configured as a fluid lens

30   OA=   optical axis

Figure 1 schematically illustrates the last lenses on the image side of a microlithography projection objective according to the invention with an immersion

fluid I, for example 25% D_3PO_4 in D_2O ($n248 \approx 1.66$), a monocrystalline last lens of NaCl, with a plane-parallel thin protector plate P or a protective layer placed in between.

5   For values of $k_1 = 0.285$, $\lambda = 248.338$ nm and a maximum incidence angle of 71.8° from the normal direction, one finds a minimum refractive index of 1.6556, a condition that is met by sodium chloride with a refractive index of 1.657766. Monocrystalline NaCl is not hygroscopic in air, in contrast to commercially available kitchen salt which contains impurities of MgCl and therefore attracts water. It should

10   be clear that the work operations on NaCl in the production process have to be free of water, because NaCl dissolves in liquid water. However, the appropriate working techniques have been known for decades. Otherwise, the lenses can be coated with vapor-deposited layers and worked on with ion beams. Inside the objective, which is normally flushed with helium or nitrogen, moisture is in any event of no concern.

15

To achieve the 32 nm node at 248 nm requires a large step in the refractive index. One finds that the refractive index needs to come up to slightly more than 2.0. At the same time, it is still necessary to obtain a satisfactory transmittance. According to the invention, the material proposed to meet these requirements is potassium iodide KI

20   with a refractive index of $n=2.0523$ at 248.338 nm.

Similar to NaCl, potassium iodide is water-soluble but advantageously isotropic. Other representatives of the alkali group in the form of iodides are likewise suitable, including NaI, RbI, CsI.

25

Since the primary use of iodides is in the infrared range, no raw materials of extreme purity have so far been used to grow crystals for the far ultraviolet range. The transmittance edge for CsI, a material of the highest refractive index, is reported as 227 nm, so that the transmittance values obtained for NaI, Ki, RbI tend to be even more

30   favorable.

The highest index of refraction is obtained with CsI as it has the highest atomic weight in the alkali group. Already at the present time monocrystalline CsI is grown and

commercially distributed for infrared applications. As a special precaution, it needs to be noted that the relative humidity of the ambient air around this crystal may not exceed 35%.

5   Figure 2 shows the end portion of a refractive or catadioptric objective with an aperture of more than 2.0. The wafer W is for example in the optical near field, with a distance of 20 nm. To show an example of a fluid lens FL, a fluid from the group of highly refractive substances that are also known as immersion fluids is arranged between the last two lenses on the image side of the objective.

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As the iodides of the alkali group are very soft and therefore mechanically delicate, it is recommended to use appropriate protective measures. Proposed is a protector plate of MgO, which has an extremely high refractive index.

15   For applications at 248 nm and other wavelengths, magnesium oxide MgO has to be produced in crystalline form with the requisite purity. In the form of a thin element, it is sufficiently transparent. The crystalline oxide material is isotropic and has a coefficient of linear thermal expansion of 14×10^{-6}/K, while CsI for example has a linear expansion coefficient of 54.9×10^{-6}/K. In order to safely join these materials by

20   wringing, it is necessary to overlay the iodide with an adhesive layer of a highly refractive material, for example hafnium oxide over CsI.

Instead of making the lenses of alkali iodide and protecting them with MgO plates, it is of course also possible to use MgO itself for the one or more last elements if a

25   crystal material of suitable transmittance and homogeneity is used. Given that MgO has very good chemical and mechanical properties and is a most highly refractive material with a refractive index over 2.0, it is suitable for the wavelength of 248 nm, if the crystal quality is appropriately optimized.

Instructive comments on this may be found in the paper by John H. Burnett et al.

30   "High Index Materials for 193 nm and 157 nm Immersion Lithography", Intl. Symp. On Immersion + 157 nm Lithography, Vancouver, 2 Aug 2004.

Figure 3 represents an example of a refractive or catadioptric projection objective in which the system aperture stop or the conjugate plane of the system aperture stop that is closest to the image plane is followed by a lens group in which the last lens and in this case also the next to last lens on the image side of the objective are lenses of

5   monocrystalline magnesium oxide.

Within the context of the periodic system of elements, MgO has a unique position.

The oxides of the first group, i.e., of the alkali group, are very unstable chemically and

10   therefore not usable. Among the oxides of the second group, the alkaline earth group, the oxide of the lightest element is BeO. While the latter has a good transmittance, it has a wurzite structure and is therefore birefringent. The further oxides MgO, CaO, SrO, BaO have the crystal structure of NaCl and are optically isotropic.

15   However, the transmittance of CaO, SrO, BaO at 248 nm is inadequate. The lightest element of the third group, boron, forms the compound B_2O_3, which is strongly hygroscopic and, by absorbing water, disintegrates into boric acid. The next heavier element, aluminum, forms sapphire crystals which are strongly birefringent. Gallium trioxide (Ga_2O_3) in both of its modifications (corundum type / monoclinic) is

20   birefringent. Indium trioxide In_2O_3 lacks transmittance already for 248 nm and is likewise birefringent.

Magnesium oxide has the further advantage of an excellent chemical stability in contact with many immersion fluids I, which necessarily should likewise have a very

25   high index of refraction at 248 nm. With a system that works in the optical near field, it is important to pay attention to the need for frequent cleaning. Using MgO in the last optical element of the system is advantageous also because of its exceptional hardness and ease of cleaning.

30   With no immediate need to push up the refractive index at the 45 nm node, it also makes sense to protect an NaCl lens with a thin MgO plate.

It is clear that objectives with aperture values of this magnitude have to be designed with extreme asphericities. It is proposed that the high-refractive elements presented above be likewise designed with aspheric surface curvatures.

5   In order to prevent the MgO element from heating up, it is important that the MgO crystal be produced from base material components of the highest purity. A certain amount of absorption can be tolerated as long as MgO serves only as a protector plate that is overlaid on another optical material, because with a small thickness of for example 1.0 mm, the absorption volume, and consequently the heat generation, will

10   remain small. If entire lenses are made of MgO, one should aim for a crystal of high purity.

The 193 nm wavelength, while not yet representing the majority of applications, is an established working wavelength and therefore, as a natural consequence, attractive for

15   a further reduction of the structure widths through the use of very large NA values.

The highest refractive indices presently used in the end-positioned elements which consist of CaF_2 or SiO_2 are:

$n = 1.501436$ for CaF_2 at 193.304 nm

20    $n = 1.560289$ for SiO_2 at 193.304 nm

Chromatic compensation materials with a higher refractive index and a higher dispersion than CaF_2 are known, e.g., from U.S. Patent 6,683,729 B1 (inventor Schuster) and from the aforementioned paper by Burnett et al., including among others

25   the following:

SrF_2 for 193.304 nm $n = 1.510219$

BaF_2 for 193.304 nm $n = 1.567043$

Thus, an objective with a large refractive lens element of BaF_2 in the end position

30   stands up better to radiation than amorphous SiO_2, but the refractive index is not significantly increased in comparison to SiO_2.

In order to safely reach the 32 nm node with the 193 nm wavelength, one needs a sufficiently high refractive index of the last lens element. For example with $k_1 = 0.265$ a refractive index of 1.658 is needed, or with $k_1 = 0.285$ a refractive index of 1.812. The photoresists for 193 already reach values as high as $n = 1.75$ in the best case.

5

A material has now been found which at 193 nm is sufficiently homogeneous and isotropic in the sense of the cubic crystal structure: Potassium chloride KCl has a very good transmittance at 193 nm and more than satisfies the requirement of a refractive index of 1.685. In fact, the refractive index of KCl is 1.756255 at 193 nm. Given that

10 the resists already reach indices up to 1.75, there is a possible application for a system where the light passes from the last lens to the resist on a wafer by means of the optical near field without immersion.

Figure 4 schematically illustrates the part of a projection objective that extends from

15 the aperture stop plane AS (system aperture plane or a conjugate plane of the system aperture plane) closest to the image field, equipped with KCl lenses according to the invention in near-field distance from a resist / wafer W.

Many applications, also at the 32 nm node, can be realized and manufactured more

20 easily with k_1 factors not quite as small as mentioned above. A second optical material has been found which meets the requirements of isotropy and transmittance at 193 nm. In addition, the refractive index is even higher.

Sodium chloride NaCl has a refractive index of 1.829085 at a wavelength of 193 nm.

25 As a result, the k_1-factor for 193 nm and for the 22 nm node can be raised again to 0.287, if one sets a maximum geometric incidence angle of 71.8°. However, with NaCl the absorption edge is slightly closer to 193 nm. Consequently, the contributions to the intrinsic birefringence are larger with NaCl than with KCl.

30 Therefore, special attention has to be paid to the compensation of the intrinsic birefringence. To compensate the intrinsic birefringence in the case of NaCl, it is proposed to join curved surfaces of NaCl lenses of different crystallographic orientation by wringing (see Figure 4).

It is likewise proposed to perform a compensation by using two different materials. Among other possibilities, this also includes combinations such as NaCl/MgO and NaCl/CaF$_2$.

Figure 5 shows an end group of a projection objective configured in this manner with a lens member made of two wrung-together KCl lens elements and as the closing member on the image side two wrung-together monocrystalline NaCl lens elements. The crystallographic orientations of the lens elements are in each case rotated relative to each other for the compensation of birefringence.

Another example is illustrated in Figure 6, where an individual KCl crystal lens is arranged in combination with an NaCl lens member of two wrung-together elements.

The coefficient of expansion is $36.6 \cdot 10^{-6}$ K^{-1} for KCl, and $39.8 \cdot 10^{-6}$ K^{-1} for NaCl. It therefore makes sense and is feasible to join the two different materials by wringing. This is shown schematically in Figure 7.

Because of its large index of refraction, NaCl should be used as the last optical element of positive refractive power. However, since larger amounts of intrinsic birefringence are present in this case, the KCl lens combines a greater refractive power with smaller intrinsic birefringence and favorable transmittance, so that the intrinsic birefringence can be compensated better and the heating of the last double lens can be kept smaller due to the reduced overall amount of absorption.

Consequently, the invention is also directed to the use of the proposed materials in 248 nm or 193 nm lithography applications; to the use of the optical near field or immersion simultaneously with the proposed materials; to the compensation of the intrinsic birefringence in NaCl at 193 nm; to the compensation of the intrinsic birefringence associated with KCl lenses; to mixed combinations in which KCl and NaCl lens elements are wrung together; to refractive indices larger than 1.75 or larger than 1.82 in lenses; to the use of chlorine compounds as a crystal material for the wavelength of 193 nm; to the location where the materials are used within the

- 10 -

objective, i.e., after the aperture stop or after a conjugate location of the aperture stop and before the image plane; to an angle of incidence on the lens surface of at least 60° and preferably larger than 70° in lenses of the proposed materials; and to the use of p-polarized light in these materials.

5

The term "lens" as used herein refers to a refractive optical element of only one material, also often referred to as lens component.

Notwithstanding any of the concepts proposed herein, this optical element can still be
10   coated, in particular with anti-reflex coatings and protective coatings against chemical and physical factors such as being attacked by aggressive chemicals, being dissolved by water or other solvents (moisture protection coating), or against scratching.

A further crystal material that has been found suitable for the lens elements of a
15   lithography objective is YAG (yttrium aluminum granate). Its chemical formula is
~~$Y_3Al_5O_3$~~ $\underline{Y_3Al_5O_{12}}$.

As a result of the yttrium content in the crystal molecules, the refractive index of YAG is higher than in MgO. In particular for 248 nm, YAG has a good transmittance. As
20   YAG has been used for many years as a material to grow high-quality crystals for lasers, and with the need to continuously improve these lasers, YAG has in the meantime been developed much farther than for example MgO or spinel $MgAl_2O_4$.

Besides spinel with an absorption edge at 160 nm and MgO with an absorption edge at
25   165 nm, YAG is another material that is still sufficiently transmissive at 193 nm.

Based on the higher index of refraction one can estimate that an absorption edge in YAG lies at about 175 nm. This makes YAG suitable as a material for lithographic projection systems for wavelengths of 248 nm and 193 nm. YAG is basically isotropic
30   but exhibits intrinsic birefringence at 248 nm and in particular at 193 nm, as is also known to occur in CaF_2 and has been described above for chloride crystals. To compensate this birefringence, it is proposed on the one hand to place at least 2 YAG-

lenses close up to the wafer or on the other hand to use a combination of YAG with MgO, or YAG with spinel, or all of the three kinds of crystals.

Figure 8 illustrates the foregoing concept schematically in an example.